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MINERAL FORMATION IN NATURAL CHEMICAL SYSTEMS UNDER EQUILIBRIUM AND NON-EQUILIBRIUM CONDITIONS*

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The processes of formation of minerals can be observed while they are going on in some cases; in most cases, however, the processes ceased before the mineral assemblages were exposed to the view of the mineralogist and geologist, and the reactions that took place can only be inferred from the nature of the mineral assemblages that they produced.

Minerals are formed in nature in many ways. They crystallize slowly from magmas deep in the earth's crust. They precipitate from hot ascending solutions. They result from the interaction of hot ascending fluids with the rocks penetrated by the fluids. The congelation of lavas poured out on the earth's surface produces mineral aggregates in some cases and volcanic glass in others. Air and rain water act upon the minerals at the earth's surface and penetrate some distance below it decomposing many minerals and carrying away part in solution. These solutions react with some of the minerals in the rocks through which they pass giving rise to additional minerals. Some of the solutions again emerge as springs and join the waters flowing on the surface in streams and rivers in which dissolved materials are carried to lakes or to the sea. From lakes and seas still more minerals are precipitated.

The crystallization of magmas in intrusive bodies proceeds slowly because the latent heat of crystallization is conducted away slowly by the overlying rocks. Laboratory investigation of many silicate systems has shown that the rate of establishment of equilibrium at liquidus temperatures is of the right order of magnitude so that in all probability approximate equilibrium is maintained between the magma of intrusive bodies and the minerals crystallizing from it at the time they crystallize. Minerals that have crystallized out in some cases react with the magma later on when they are no longer stable in contact with it; in other cases they persist unchanged, although with further cooling of the magma they

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are no longer in equilibrium with it and should change in composition or be redissolved. Incompletely resorbed crystals of olivine and zoned crystals of feldspar and pyroxene in many rocks indicate that the minerals did not maintain perfect equilibrium with the magma after their formation.

Insofar as the crystallization of a particular portion of magma proceeds with approximate maintenance of equilibrium between the magma and the crystals forming from it, the process can be represented approximately by a line or curve in an equilibrium diagram. If some of the crystals are removed from the portion of the magma under consideration by sinking or floating, the further course of crystallization of the remaining portion can still be represented by a line or curve in an equilibrium diagram, but plotting the further course of crystallization is only possible if the mass of the crystals removed is known as well as their composition. The use of equilibrium diagrams to portray processes in which the mass of the system is changing is possible because the changes of state of a system of variable mass are represented by a definite path in the equilibrium diagram provided the mass subtracted or added is in equilibrium with the solution at the time it is subtracted or added. If crystals once formed become unstable in relation to the magma when the temperature falls, but fail to react with the magma because they are separated from it by a protective coating, it would be necessary to know the mass and composition of the crystals so separated in order to plot precisely the further course of crystallization of the remaining magma. Without knowledge of the mass of crystals removed from the magma or separated from it by protective coatings it would still be possible, however, to tell the general nature of the deviation of the further course of crystallization from the path that would have been taken if no crystals had been removed or separated by protective coatings, provided the composition of the crystals removed from the magma or separated from it is known.

As a result of investigations of equilibrium relations in silicate systems it has become generally accepted that the larger scale field and smaller scale microscopic relations of the igneous rocks are in many cases interpretable as the results of crystallization during which the reaction relations of many of the minerals and the differing extents to which equilibrium was maintained brought about a diversity of mineral assemblage in the intrusive igneous rocks even from initially similar magmas.

Liquid magma poured out on the earth's surface as lava from fissures or vents in some cases cooled slowly enough so that it became completely crystalline, but in other cases it congealed to a mixture of crystals and glass; in still other cases lava masses solidified as almost completely glassy rocks. The series of states through which the magma passed as it changed from a liquid to a glass were non-equilibrium states and the process cannot be represented by a curve in an equilibrium diagram.

During the crystallization of magmas in deep seated intrusions the residual fluid became enriched in water and other constituents not present or present to a very limited extent in the early formed crystalline phases. The resulting fluids in part crystallized within the intrusive bodies where they formed pegmatitic masses grading into the surrounding rock of the intrusive. In part the residual fluids were forced into the rocks surrounding the intrusive along fissures or planes of weakness and there formed pegmatite dikes. During the crystallization of the pegmatitic masses and dikes the minerals crystallizing out of the fluid may well have been in approximate equilibrium with the fluid at the time they crystallized; the large crystals found in pegmatites are regarded as indications that growth proceeded for a long time without large changes of temperature, pressure or concentration. Moreover, it has been found in laboratory experiments with related systems of silicates and water that equilibrium is rather rapidly established at temperatures and pressures near those that obtained during the crystallization of pegmatites. As the character of the solutions changed, however, some of the early formed minerals became unstable and were replaced by others, but the alterations in the crystalline phases probably did not always keep pace with the changes in the fluid phases. Some minerals although unstable have persisted in part until exposure of the pegmatitic masses and dikes by erosion.

Adams[1] has stated that for an understanding of pegmatite formation data on the equilibrium relations in the very complex system Na_2O-K_2O-Al_2O_3-SiO_2-H_2O at temperatures below about 600° C are needed. Although data for this quinary system are not yet available, investigations of the equilibrium relations in the systems Na_2O-SiO_2-H_2O and K_2O-Al_2O_3-SiO_2-H_2O are being conducted at the Geophysical Laboratory and it is hoped will lead to a determination of the equilibrium relations in the part of the quinary system that is of interest for its application to pegmatite genesis. Data for the ternary systems Na_2O-Al_2O_3-SiO_2 and K_2O-Al_2O_3-SiO_2, which are parts of the quinary system, were published by Schairer and Bowen[2] several years ago, and very recently the results of the comprehensive study of the system $NaAlSi_3O_8$-$KAlSi_3O_8$-H_2O by Bowen and Tuttle[3] appeared. At high temperatures soda feldspar and potash feldspar form a continuous series of solid solutions of the type with a minimum melting temperature at an intermediate composition in the series.[4] The diagram is complicated toward the potash-rich side by the incongruent relations resulting from the

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[1] Adams, L. H., Carnegie Institution of Washington Yearbook, No. 38 (1939) page 38.

[2] Schairer, J. F., and Bowen, N. L., *Am. Jour. Sci.*, **245**, 193–204 (1947).

[3] Bowen, N. L., and Tuttle, O. F., *Jour. Geol.*, **58**, 489–511 (1950).

[4] Schairer, J. F., *Jour. Geol.*, **58**, 512–517 (1950).

separation of leucite. In the presence of water vapor under pressure Bowen and Tuttle found that the melting temperatures are lowered substantially and they determined the precise values of the lowering at several pressures. At temperatures below the melting curve at the pressures used the homogenous feldspar that crystallized from the melts unmixes, a relation that was deduced from study of natural perthites by previous investigators. The actual position of the unmixing curve or solvus was determined by Bowen and Tuttle. Unlike the liquidus and solidus curves, the solvus does not change its position measurably with change of pressure of water vapor because water does not participate in the equilibrium at the solvus.

Other residual magmatic fluids deposited metallic ores with accompanying gangue minerals in the adjacent and overlying rocks as well as in parts of the magma already congealed. The composition and state of these fluids in depth can only be inferred from the nature of the deposits that precipitated from them or resulted from their interaction with the rocks invaded by them. Careful field and microscopic study of deposits formed in depth has yielded some knowledge of the chemical elements carried by the ore-forming fluids. From observations of the structures and textures of the deposits and of the minerals formed, various suggestions have been made by ore geologists as to the physical character and chemical composition of the ore-forming fluids, but considerable uncertainty and difference of opinion remain on these points. That the attack on the difficult problems of ore genesis should begin with carefu and accurate mapping and recording of the geologic features of ore deposits, including structures, textures, mineral associations and alteration of enclosing or adjacent rocks, has been emphasized by numerous investigators and seems beyond dispute. Mining geologists are concerned most of all with the structural features of ore deposits, since the location, size and shape of ore bodies depend so much on structural factors. However, such experienced and eminent ore geologists as Butler, Hewett, Sales, Locke, Ransome, Graton and Blanchard have concluded that field studies need to be supplemented by laboratory investigations in order that a better understanding may be obtained of the chemical aspects of ore deposition.

A number of studies of solubilities of ore minerals have been carried out in recent years and have yielded some valuable information. The importance of determinations of sulfide solubilities in systems containing silica and various other components that are believed to have been present in the ore-forming solutions (since quartz and various other gangue materials were deposited along with the sulfides) is undoubtedly great. It appears that in order to obtain an understanding of the ore mineral associations, systematic determinations of the phase equilibria in a number of systems made up of the constituents of ores plus water, H_2S, H_2SO_4, CO_2, Cl_2, F_2, etc., should be undertaken. It might then be possible to deduce from the equilibrium diagrams of such systems some of the series of minerals that would be precipitated by the cooling of solutions in such systems or by their reaction with wall rocks or by the lowering of external pressure. If a particular mineral association and sequence could be shown to result from one of these solutions by cooling, reaction or pressure release, we would then have stronger evidence than is now available that the hypothetical solution was approximately like the actual ore solution responsible for the natural ore deposit. The needed equilibrium investigations, although difficult and laborious, do not appear to be entirely beyond the range of present technical resources. The determination of homogeneous equilibria, that is, the molecular and ionic groupings in the solutions under equilibrium conditions, would not necessarily have to be carried out. The determination of the heterogeneous equilibria alone, that is, the compositions of the fluid and crystalline phases in equilibrium at the various temperatures and pressures in certain systems might be found sufficient to throw considerable light on the conditions of formation of the ore minerals and the nature of the ore fluids. The system hydrogen-oxygen-sulfur and the system hydrogen-oxygen-sulfur-iron are two that were recommended for investigation by the National Research Council Committee on Problems of Ore Deposits[5] in 1940 as fundamental to the further understanding of the chemistry of ore deposition. The equilibrium of the solid phases and vapor phase in the system copper-iron-sulfur was the subject of a comprehensive study by Merwin and Lombard.[6] Their work was carried out at a series of vapor pressures up to the melting curve. If the heterogeneous equilibria in the system hydrogen-oxygen-sulfur-iron were determined in the temperature-pressure-concentration range relevant to ore formation problems, the results of Merwin and Lombard would then provide a basis for extending the equilibrium data to the system hydrogen-oxygen-sulfur-iron-copper in the relevant temperature-pressure-concentration range. Knowledge of the equilibrium relations in this system would certainly be of great interest for its bearing on the hypogene mineralization of the porphyry copper deposits.

The quicksilver deposits are among the hydrothermal deposits believed to have formed at relatively low temperatures and pressures. They have been carefully studied in the field and their structural and mineralogical

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[5] Report of the Committee on Problems of Ore Deposits, National Research Council, Washington, D. C. (1940) (Mimeographed Draft).

[6] Merwin, H. E., and Lombard, R. H., *Econ. Geol.*, **32**, 203–284 (1937).

features have been well described. The simplicity of the mineralogy and the probability that they were formed at shallow depths by solutions not very different from hot spring waters such as those now emerging at Steamboat Springs, Nevada, should make it possible to deduce the main features of the processes by which they originated, with less difficulty than would be the case with most metalliferous deposits. According to Brannock, Fix, Gianella and White,[7] at Steamboat Springs the hot waters are now depositing fine grained dark-gray to black mud at the surface, consisting mainly of particles believed to be silica gel or opal and containing stibnite and pyrite and appreciable amounts of gold, silver, mercury and antimony in undetermined form. A large quantity of originally porous sinter at Steamboat Springs that is now buried under younger sinter has been reworked by the hot waters after burial and filled with opal, chalcedony, and some quartz. Radial clusters of stibnite occur in small cavities and embedded in opal in the reworked sinter. Fine-grained cinnabar also is found in many parts of the reworked sinter.

Analyses of the waters of the springs indicate a parent saline magmatic water diluted to varying degrees by meteoric water of low concentration. The water in the different springs at Steamboat Springs ranges from slightly acid to moderately alkaline and on the average is slightly alkaline. The acidity or alkalinity of the water appears to be related to the temperature of the spring, with the most alkaline waters tending to be those issuing at the highest temperatures.

In the Goldbanks District of Nevada a commercially productive cinnabar deposit was formed syngenetically with a silica apron deposited by thermal springs, according to Dreyer.[8] Many of the opalitic cinnabar deposits are stated by C. P. Ross[9] to have been formed within a few score or at most a few hundred feet of the surface, and in a few, such as those of the Coso District of California, the cinnabar crystallized in hot springs at the surface. Many other types of quicksilver deposit have been described in the United States, but all appear to have been formed close to the surface and at relatively low temperatures.

It has long been known that mercury sulfide is appreciably soluble in alkaline sulfide solutions. The solubilities of cinnabar were determined by Knox[10] for a range of Na_2S concentrations at 25° C and 33° C. Knox's equilibrium investigations showed that an increase in the concentration of Na_2S in the solution causes an increase in solubility of cinnabar in the

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[7] Brannock, W. W., Fix, P. F., Gianella, V. P., and White, D. E., *Trans. Am. Geophys. Union*, **29**, 211–226 (1948).

[8] Dreyer, R. M., *Econ. Geol.*, **35**, 141–145 (1940).

[9] Ross, C. P., *Econ. Geol.*, **37**, 461 (1942).

[10] Knox, J., *Zeit. f. Elektroch.*, **12**, 477–481 (1906).

system HgS-Na_2S-H_2O. That the mercury sulfide of the quicksilver deposits was transported in alkaline sulfide solution has been generally accepted by geologists who have studied these ores. There is not such complete agreement, however, as to the relative importance of several possible causes of the deposition of the cinnabar. The causes to which the precipitation of the cinnabar has been ascribed are chiefly evaporation of solution into open spaces in the wall rock, reaction of the solution with the wall rock, reduction of the alkalinity of the solutions by admixture of acid meteoric waters, dilution by neutral meteoric waters, cooling of the hypogene solutions, and decrease of pressure. From Knox's data it may be concluded that dilution and evaporation are probably among the less important of these factors. Some quicksilver deposits contain metacinnabar as well as cinnabar, but others are devoid of metacinnabar. Allen, Crenshaw and Merwin[11] showed that metacinnabar precipitates from acid solutions under certain conditions. Its presence in some of the quicksilver deposits can be ascribed to acidification resulting from admixture of acid meteoric waters and/or to the oxidation of H_2S of the hypogene solutions by air oxygen close to the surface. Allen, Crenshaw and Merwin proved that cinnabar is the stable modification of mercuric sulfide over the whole temperature range up to the volatilization point (at atmospheric pressure). The deposition of metacinnabar in some quicksilver ores is thus an example of metastabile phase formation. At the time it precipitated from the ore solutions the metacinnabar was probably in metastabile equilibrium with those solutions. In some of the ores in which it has been found the metacinnabar has partly changed into cinnabar according to Dreyer,[12] probably as the result of an influx of additional hypogene alkaline sulfide solution.

In numerous quicksilver deposits the cinnabar is associated with silicified gangue; the silicification is in part much older than the cinnabar; in part the silicification and cinnabar deposition went on together as indicated by the very fine dispersion of much of the cinnabar in the quartz and chalcedony. The association of cinnabar with quartz, chalcedony and opal can be understood in a general way, since silica is appreciably soluble in solutions containing alkaline sulfide of mercury. Investigation of the equilibrium relations in a certain temperature-pressure-composition range in the system HgS-Na_2S-Na_2O-SiO_2-H_2O might provide the basis for a more detailed understanding of the paragenetic relations. Knox's[13] determination of the saturation surface of cinnabar in the system HgS-Na_2S-Na_2O-H_2O would provide a starting

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[11] Allen, E. T., Crenshaw, J. L., and Merwin, H. E., *Am. Jour. Sci.*, **34**, 341–396 (1912).

[12] Dreyer, R. M., *Econ. Geol.*, **35**, 149 (1940).

[13] *Op. cit.*

point for the investigation of the equilibrium relations in the relevant part of the system HgS-Na_2S-Na_2O-SiO_2-H_2O. The association of cinnabar with other minerals, calcite, dolomite, pyrite, marcasite, kaolin group minerals, etc., is probably not as close in the main as its association with silica minerals. Some chemical aspects of these other associations have been discussed by several investigators, but not from the point of view of heterogeneous equilibria, necessary experimental data for such discussion not having been determined.

When ore deposits become exposed by erosion they are attacked by meteoric waters and atmospheric oxygen and carbon dioxide. At the surface and downward for a distance varying in different deposits the sulfide minerals usually are oxidized. Observation of oxidation products in outcrops impels the mining geologist to ask from what minerals were they formed and how much of the unoxidized minerals exists below. The importance of oxidation products in outcrops as possible indicators of unoxidized ore beneath has led to field and laboratory investigations aimed at better understanding of the oxidation of the sulfide minerals.

The disseminated copper deposits of the southwestern United States are relatively simple in mineral make-up. They consist chiefly of finely distributed pyrite, chalcopyrite, chalcocite and covellite in altered monzonite porphyry or altered granite porphyry or altered schist. As a result of the alteration of the original igneous or metamorphic rocks associated with the introduction of the copper, the ore bodies are crackled masses of fine-grained quartz and sericite together with fine-grained biotite and alunite and kaolin group minerals, through which the sulfides are disseminated in veinlets and in individual grains replacing the rock between the finest veinlets. The oxidized cappings above the ore bodies contain hematite, goethite, jarosite and nontronite in the veinlets and spaces where the sulfide minerals were before oxidation; the hematite, goethite and jarosite also are scattered through the surrounding rock as replacements of the sericite, kaolin group minerals and quartz. In some places important quantities of azurite, malachite and chrysocolla remain in the cappings, but in most places the copper has been leached from the cappings and carried downward in solution.

The reasons why iron minerals and copper minerals are in some places deposited in the cappings during oxidation whereas in other cases practically all of the copper and some of the iron are carried downward in solution are now fairly well established as a result of field and microscopic study together with laboratory determinations of the equilibrium relations in the relevant part of the system CuO-Fe_2O_3-SO_3-H_2O[14] and

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[14] Tunell, G., and Posnjak, E. W., *Jour. Phys. Chem.*, **35**, 929–946 (1931).

supplementary experiments on equilibria[15] and reaction velocities.[16] The products formed and the quantities of each when given quantities of iron and copper sulfides are oxidized in a given quantity of water can be calculated from the equilibrium diagram of the system CuO-Fe_2O_3-SO_3-H_2O provided all the iron be oxidized to the ferric state. It is noteworthy that the deposition of tenorite or brochantite or antlerite will only take place after practically all the iron (ferric) is precipitated as goethite or $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. In order that all of the iron as well as all of the copper remain in solution a higher concentration of $SO_3(H_2SO_4)$ is required. In the oxidation of the disseminated copper ores the sericite is slightly attacked by the acid solutions. The small amount of potash taken into solution from the sericite plays an important role in the formation of hematite and jarosite as in its absence only goethite and

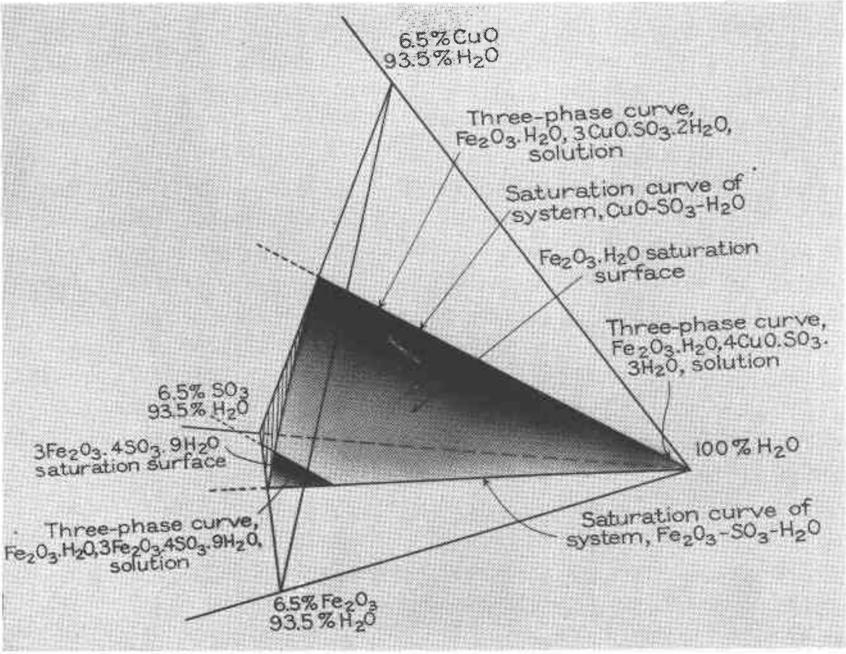

FIG. 1. Perspective view of a model of the isothermal-isobaric saturation surface in the portion of the system Fe_2O_3-CuO-SO_3-H_2O in which the total composition is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3.

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[15] Posnjak, E., unpublished work.

[16] Posnjak, E., *Amer. Inst. Min. and Met. Eng.*, Pamphlet No. **1615D** (issued with *Min. and Met.*, December, 1926).

$3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ would be formed. That a very small concentration of potash causes the formation of jarosite in a solution that would otherwise precipitate $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ was proved experimentally by Posnjak.[17,18] The small amount of potash yielded by the decomposition of sericite is not sufficient, however, to cause the deposition of hematite where the total percentage of sulfides in the ore is moderate to high and where the ratio of pyrite to chalcocite and/or covellite is high. In the oxidation of such ore or protore goethite and jarosite precipitate. Oxidation of the disseminated copper ores appears to have been approximately thorough in some places, but in other places it was not thorough. The effect of non-thorough oxidation, in which some ferrous sulfate is present, is to diminish the quantities of goethite and/or jarosite precipitated, because there is less ferric sulfate and more sulfuric acid present. The knowledge gained of the chemical aspects of the oxidation process provides an explanation of the fact observed by Ransome[19] that copper-stained rock traversed by many little veinlets of chrysocolla is abundant in the Miami District of Arizona, but as a rule the best ore bodies do not occur beneath rock of this character. Ransome inferred that the process of supergene enrichment is far more active when the material undergoing oxidation contains abundant pyrite than when it is chiefly chalcocite.[20] He observed that in the weathering of chalcocite, especially in feldspathic rocks, part of the copper is not carried downward as sulfate, but is converted into carbonate or silicate and remains near the surface. Ransome's observations of several features of oxidized cappings were very acute, and his conclusions concerning their significance in terms of underlying ore and waste were well founded and foreshadowed the results of later investigations.

I shall not proceed to discuss other types of mineral assemblage. I have attempted to indicate some of the controlling factors in the forma-

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[17] Unpublished work.

[18] Jarosite and $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ appear to have closely similar structures with one water molecule of $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ taking the place of a potassium ion of jarosite and a second water molecule of $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ taking the place of a hydroxyl ion of jarosite (S. B. Hendricks, *Am. Mineral.*, **22**, 780 (1937)).

[19] Ransome, F. L., *U. S. Geol. Surv.*, *Prof. Paper No.* **115**, p. 164 (1919).

[20] *Op. cit.* p. 171. (This conclusion of Ransome was an important advance in the understanding of leached outcrops. Ransome's comment on the same page regarding the statement of Zies, Allen and Merwin that sulfuric acid retards but does not change the nature of the reaction between pyrite and cupric sulfate resulted, however, from his failure to note that Zies, Allen and Merwin explicitly limited their discussion to the enrichment process alone as contrasted with the combined oxidation-solution-transportation-enrichment process to which Ransome applied their statement. The statement of Zies, Allen and Merwin is entirely correct in the case to which they clearly limited it.)

tion of just a few types. Field and microscopic investigations of the rock bodies and mineral deposits constituting the mineral assemblages discussed had inevitably raised the question: why are the particular minerals associated in the particular structures and textures? In some cases a partial answer to this question has been found through experimental determinations of heterogeneous equilibria and reaction velocities.

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